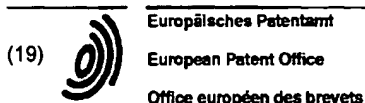


MACHINE ASSISTED TRANSLATION



(11) **EP 0 530 538 B1**

EUROPEAN PATENT

(45) Publication date and disclosure of the
 announcement of the patent grant:
 05.02.1997 Patent Journal 1997/06

(51) Int. Cl.⁶: **B32B 27/08**, B32B 27/34,
 B65D 65/40

(21) Application number: 92113527.3

(22) Application date: 08.08.1992

(54) 5 layered coextruded biaxially oriented tubular film with at least 3 polyamide layers

(84) Designated contracting states:
 AT DE DK IT FR GB IT NL

(30) Priority: 23.08.1991 DE 4128083
 13.09.1991 DE 4130486

(43) Publication date of the application:
 10.03.1993 Patent Journal 1993/10

(73) Patentee: Wolff Walsrode Aktiengesellschaft
 D-29655 Walsrode (DE)

(72) Inventor:
 • Hennig Cardinal of Widdern, Michael, Dipl.-
 Ing. W-3030 Walsrode (DE)
 • Weber, Gunter, Dr.
 W-3032 Fallingbommel (DE)

(74) Representative: Brown, Rolf, Dr.
 Bayer AG
 Company Administration RP
 Patent Department
 51368 Leverkusen (DE)

(56) Prior art:
 EP-A 0,132,565 EP-A 0 225 164
 EP-A 0,277,839 DE-A-4 001 612
 USA 4,668,571
 • Derwent Publications Ltd., London, GB
 • Derwent Publications Ltd., London, GB;

Note: Anyone can submit an objection with the European Patent Office against the grant of the European patent within nine months after the publication of the notice of the grant of the European patent. The objection is to be submitted in writing and documented. It is only considered as having been submitted if the objection fee has been paid. (Art. 99(1) European Patent Convention).

Description

The invention concerns a coextruded, biaxially stretched tubular film for encasing contents packaged in a liquid or pasty state, in particular foodstuffs, such as boiled sausage, cooked sausage and processed cheese, in a long-lasting manner, free of creases,.

Casings for foods, e.g. cooked sausage or boiled sausage or filling materials packaged by means of the same or a similar process must fulfill an extensive set of requirements in order to be applicable in practice.

These requirements are:

a) Resiliency

A volume reduction of the packaged material occurs both on cooling of the previously heated contents and with the weight loss due to the evaporation of water during storage. Independent of the volume reduction, the film must fit around the contents wrinkle-free, in order to provide to the material with a sales promoting appearance.

b) Strength

The contents are compressed into the tubular film at high speed, with a filling pressure of up to 1.6 bar. After it is subjected to pressure, the film material should exhibit neither partial expansions (dents) nor a substantial expansion of its caliber (diameter). It must be ensured via the film quality that the high filling pressure primarily leads to a flexible deformation of the tubular film.

c) Temperature stability

The casing must withstand a temperature/stress load in such a manner that it withstands the pressure of the contents, even during the cooking procedure, without excessive deformation.

d) Barrier properties

For purposes of the intended application of the tubular film as, among other things, a casing for boiled and cooked sausage, good barrier properties regarding oxygen and water vapor permeation are required.

The oxygen barrier prevents an early discoloration of the cooked meat next to the film.

The water vapor barrier obstructs the decrease in the weight of goods that are sold as induced by the evaporation of water from the filling, which on the one hand reduces proceeds from the product and on the other hand can lead to wrinkled, unattractive products due to the volumes loss.

e) Adhesion of the cooked meat

The tubular film must exhibit adhesion of the contents, particularly for application as a boiled sausage and cooked sausage casing. Adhesion of the cooked meat is understood by the specialist to mean the adhesion property of the casing to the contents. The affinity between the casing and the contents prevents the deposition of jelly.

f) Transportability

Before industrial processing by means of automatic filling machines, the tubular film is transported in the form of a gathered caterpillar. The tubular film is folded along the tubular axis and then compressed with a ratio of 30:1 to 60:1. The film must withstand the extremely high breaking stress without damage.

g) Foodstuff laws

The product may naturally contain only materials that are classified as harmless according to the food laws and recommendations.

h) Ecology

The product should consist only of materials that are harmless from an ecological viewpoint in their production, processing and application, and in their disposal.

No biaxially stretched tubular films made of thermoplastic synthetic materials, which meet this extensive set of requirements in all respect have been known until now. The constantly progressing separation of chlorine-containing packaging forces manufacturers and processing plants of synthetic gut casings made of VDC/VC copolymers to offer alternative packing solutions. Since the stretched film made of VDC/VC copolymer could only fulfill the requirements regarding "strength", "oxygen barrier", "water vapor barrier" and "cooked meat adhesion" via a polymer, the film manufacturers were ready to pay a relatively high price for the VDC/VC copolymer raw material. On the other hand, the ongoing development of coextrusion

technology now allows for a combination of polymer characteristics in the coextrusion laminate using more inexpensive polymers.

The manufacturers of tubular films are interested in producing a product meeting the quality demands of the users as reliably and inexpensively as possible in order to, on the one hand, reduce the waste rate as much as possible and to be able to supply a reproducible films quality and, on the other hand, to be able to offer a highly improved product inexpensively.

The known production process for biaxially stretched tubular film is divided into the following process steps:

- Plasticization of the thermoplastic polymers
- Conversion of the melt into the tubular form
- Rapid cooling of the melted liquid primary tube to the solid state in order to as much as possible suppress the formation of crystallites
- Reheating of the primary tube to a temperature suitable for biaxial stretching
- Biaxial stretching of the reheated primary tube by applying a pressure difference between the interior volume of the tube and the tube exterior and by applying longitudinal drawing force in support of the longitudinal stretching
- Thermofixing of the biaxially stretched tubular film
- Rolling up the tubular film
- Various manufacturing steps depending on subsequent requirements (e.g. cutting, printing, gathering up and the like)

The specialist understands biaxial stretching to mean transverse and longitudinal stretching of the thermoplastic extrudate at temperatures between the glass transition temperature and the melt temperature. Biaxial stretching can for example take place by means of a bubble filled with a gas or a fluid pressurizing pad, which is enclosed in a gas and/or fluid tight manner between two pairs of rollers running with different peripheral speeds. While the ratio of the different peripheral speeds of the rollers corresponds to the degree of longitudinal stretching, the transverse degree of stretching is calculated from the ratio of the tube diameter in the stretched state to that in the unstretched state. The planar degree of stretching is given by the product of the degree of longitudinal stretching times the degree of transverse stretching.

During stretching, the molecules orient themselves in the solid state of the tubular film so that the elastic modulus and the strength are substantially increased.

Sufficient strength the tubular film is attained if the package casing is noticeably elastically deformed during the filling process and during sterilization. The package casing must retain its cylindrical form and may not form bumps or bends.

The biaxial stretching of tubular films made of partially crystalline thermoplastic polymers, e.g. polyamide, polyvinylidene chloride, requires rapid cooling of the melted liquid primary tube, since the resulting crystalline superstructure otherwise obstructs the subsequent biaxial stretching. The inhibition of biaxial stretching shows up in practice as an unstable stretching bubble, i.e. the neck of the stretching bubble moves in varying directions along the tubular axis, with the consequence that the tubular diameter of the final product becomes uneven.

The patent literature provides numerous references regarding the processing of partially crystalline, aliphatic polyamide (PA) to produce biaxially stretched films and their subsequent use as boiled and cooked sausage casings. Both technical solutions for the production process of the biaxially stretched tubular films and the development of formulations for improved applied technical properties have been published therein.

DE 2 850 181 indicates that an improved stretchability can be achieved by mixing olefinic copolymers into the PA. According to the information from the patent owner, this is evidenced by the fact that a visually clearly ascertainable uniformity of the stretching bubble is achieved and a substantial reduction of the required stretching forces is furthermore observed.

The water vapor barrier of films with a PA matrix can be clearly improved by mixing in olefinic (co)polymers or other polymers, which exhibit a lower water vapor permeation than aliphatic polyamides; however, the water vapor barrier must be considered to be insufficient and thus in need of improvement compared with casings of PVDC copolymers. Difficulties regarding a constant product quality frequently occur in the processing of polymer blends, since the distribution of the blend components in the matrix has a considerable effect on the stretchability and the barrier properties. Due to the fact that the quality of the distribution depends on very many processing parameters (e.g. the viscosities of the blend partner, the processing temperatures, the stretching rates, the screw geometry, etc.), the production of a reproducible product quality is extremely difficult.

The attainable improvement of the water vapor barrier of single layered tubular PA films by means of the use of blending technology results from the planar intercalation of blend components in the PA matrix. The size of the intercalated areas is in particular affected by the degree of biaxial stretching of the film.

However, the planar intercalation does not give a closed films layer and accordingly cannot reduce water vapor permeation to the extent possible with the use of coextrusion technology. This means that, through the application of coextrusion technology, a clearly improved water vapor barrier is attained while using the same material. This provides economic and ecological benefits.

Similar methods of operation are described in EP 0 216 094 and DE 3 801 344.

In accordance with EP 0 216 094 one achieves an improved oxygen barrier with a simultaneous high permeability to smoked taste carriers by admixing ethylene-vinyl alcohol copolymers (EVOH) to the PA. Apart from the aforesaid difficulty in obtaining a reproducible product quality, the insufficient temperature stability of EVOH during mixing with polyamides, which are processed at high temperatures, leads to an unwanted decomposition of the EVOH.

DE-OS 3 801 344 describes a biaxially stretched tubular film made of a ternary blend. While the principal weight fraction of the film consists of aliphatic PA, further fractions of polyterephthalic acid esters and aromatic PA are added. According to specifications of the applicant, the goal of these blend structures is a homogeneous color pigment distribution in the film, which can be achieved by formulating a master dye batch with the aromatic PA and subsequent mixing.

Like all of the aforesaid monolayer films based on aliphatic polyamides, this film structure also fulfills neither the manufacturer's requirements nor the requirements of the processing plants for a high barrier effect toward water vapor and oxygen permeation.

The quality of the tubular film demanded on the part of the users can only be fulfilled from an economic and ecological viewpoint via coextruded, stretched tubular films.

In the Japanese application J 1 014 032 a biaxially stretched, coextruded tubular film is described for use in cooked meat and cooked sausage casings consisting of 3 layers, with the outside layer turned away from the filling material consisting of an aliphatic PA and the inner layer of ethylene-acrylic acid copolymer. The middle layer consisting of PP and/or PE copolymers and located between the external and internal layers serves as an adhesion enhancer. The internal polymer layer of ethylene-acrylic acid copolymer takes on the function of cooked meat adhesion. In accordance with a subsequent patent application, GB 2 205 273, the cooked meat adhesion of the internal LLDPE layer is improved by means of a costly corona pretreatment acting on the inside of the tubular film.

It is the aim of this invention to make an ecologically compatible, biaxially stretched tubular film with an improved barrier effect and improved application technical properties available to the user.

The object of this invention is an at least five-layered, coextruded biaxially stretched tubular film for encasing contents, in particular foodstuffs, packaged in a liquid or pasty state, which, due to its barrier effect against water vapor and oxygen, durably covers the filling in the filled state for prolonged storage times, without forming creases and without an observable oxygen effect, whose tubular interior layer facing the filling exhibits cooked meat adhesion, characterized by the fact that it is composed of at least 3 PA layers, which constitute the core layer, the internal and the external layer.

The high oxygen barrier of the coextruded tubular film of this invention results from the multilayer positioning of the individual PA layers. This phenomenon can be reproduced in a simple experiment, e.g. in which a 60 µm thick, monolayer PA6 film is compared with a three-layered 60 µm thick film (3 x 20 µm) regarding the O₂ barrier. The explanation for this phenomenon probably lies in the interaction of boundary surfaces and the molecular superstructure that is formed as a consequence of the production method involving biaxial stretching and subsequent annealing.

Oxygen penetration causes discoloration of the cooked meat at the surface of the boiled or cooked sausage which is visible to the consumer. Advanced discoloration imparts a sales restraining appearance, which particular comes into play if goods with different production dates lie close together on the store shelf.

Aliphatic amides, such as polyamide-6 or copolyamides with a predominant fraction of caprolactam are used in a preferred embodiment. These polyamides can be processed alone or as a polymer mixture with each other or as a polymer mixture with other polymers, e.g. aromatic polyamides PE (copolymers), PP (copolymers), polyester, etc., with a predominant PA fraction.

It is easily possible to further improve the oxygen barrier of this PA laminate by

1. allowing one or two of the three PA layers to consist of partially aromatic PA
2. inserting one or two EVOH layers between the three PA layers.

In a preferred embodiment, at least one olefinic layer, which inhibits water vapor permeation, is inserted between the PA layers. This layer has an adhesion mediating effect on the PA and consists of copolymers based on ethylene or propylene with functional groups. In a particularly preferred embodiment, this layer is inserted between the internal and the core layer. In the case of very high demands regarding the water permeation barrier, this kind of olefinic layer can also additionally be inserted between the internal and the core layer.

By inserting the olefinic polymer layers, the outside PA layers are in addition protected against the penetration of cooked meat juices. This entails a further improvement of the oxygen barrier.

In practice, tubular casings are hydrated before they are processed by means of fast automatic filling machines. Aside from surface wetting of the tubular casing, it is the goal this process step to improve flexibility through water take-up. Tubular films of thermoplastic materials are also subjected to this treatment in order to, among other things, make polymers that are capable of taking up water "soft" by storing water. In the case of aliphatic polyamides, the range of the glass transition temperature can be lowered to below 0°C as a consequence of water take-up.

In the tubular film of this invention, 2 of the 3 PA layers are located in the external and respectively the internal positions, in order to ensure unimpaired water take-up during the hydration process.

In a particularly preferred embodiment, the PA in the internal core layer is a copolyamide layer with a predominant caprolactam content or a partially aromatic PA layer, since the effect of water take-up by these polymers is of only minor significance. This is particularly so if the PA core layer is totally encapsulated by olefinic water vapor barriers.

Examples

The examples listed below were realized with a 5-layered tubular coextrusion line. The plasticizing and the homogenization of the polymers that are employed occurred by means of 5 separate extruders.

In those cases in which the film laminate was formed with less than 5 polymer layers (with changing polymers compositions), identical polymer types were placed next to each other.

Example 1

The polymer (A1) is plasticized and homogenized through 5 extruders and is converted to the tubular form by means of a 5-layer coextrusion nozzle. The tubular films therefore have the structure: A1/A1/A1/A1/A1

- The polymer A1 is a polyamide 6 (B40 F from Bayer AG).

The tubular shaped coextrudate exiting from the nozzle is also covered both on the outside and on the inside with water at a controlled temperature of 10°C. The cooling water on the inside of the tube is squeezed out by tightly fitting rollers. This pair of rollers simultaneously takes on the function of drawing off the melt from the nozzle. The complete removal of the residual moisture from the external surface of the primary tube is accomplished by means of a mechanical wiping device and an air jet. The unstretched primary tube obtained in this manner has a diameter of 20 mm and a total layer thickness of 500 µm.

After it is reheated to a temperature of 90°C, the primary tube is stretched 3.0-fold in the transverse and 3.0-fold in the longitudinal direction by inclusion of an air bubble between two roller pairs with different peripheral speeds.

Again between two tightly fitting roller pairs, the biaxially stretched tubular films pass for 15 seconds through a heat treatment zone (thermosetting) at a controlled temperature of 160°C, while a gas pressure pad acting from the inside prevents shrinkage as much as possible. The resulting biaxially stretched, heat treated tubular film has a total layer thickness of 56 µm.

With a flat lying width of 85 mm, the flat lying width fluctuation of the flat lying tubular films was less than 1.0 mm for an observation period of 30 minutes.

During the subsequent application technical test, the tubular film is, after 10 minutes of storage in water at a controlled temperature of 20°C, filled with liver sausage, scalded for 45 minutes at 75°C, showered with cold water and completely cooled in cold-storage. The tubular film encases the sausage meat smoothly and tightly and displays good meat adhesion properties.

The weight losses due to the evaporation of water over a storage time of 20 days are 1.2 wt-%; the side of the liver sausage facing the film experiences no discoloration.

The film can be very readily peeled helically from the filling.

Example 2

In example 2, the core layer A1 of example 1 is replaced by a partially aromatic PA and the internal layer A1 by a copolyamide 6.66. This results in the structure (from the outside in): A1/A1/A2/A3/A3

- Polymer A1 is an aliphatic polyamide 6 (B40 F from the Bayer AG),
- Polymer A2 is a partially aromatic PA (Nyref N-MXD6 from Solvay),
- Polymer A3 is an aliphatic copolyamide 6.66 (Ultramid C 35 from BASF AG).

A primary tube with the following layer thickness distribution is produced with same operational sequence as in example 1:

A1 = 135 μm , A1 = 65 μm , A2 = 90 μm , A3 = 65 μm , A3 = 135 μm .

The biaxially stretched, heat treated tubular film has a total layer thickness of 57 μm .

With a flat lying width of 85 mm, the flat lying width fluctuation of the flat lying tubular film is less than 1.3 mm for an observation period of 30 minutes.

The weight losses through evaporation of water over a storage period of 20 days are 1.0 wt-%; the side of the liver sausage facing the film experiences no discoloration.

In other respects, this film structure achieves equally good results in the application technical tests as the one from example 1.

The summary of the most important application technical results is listed in Table 1.

Example 3

Based on example 1, an olefinic copolymer is inserted between the individual PA layers thereby giving the following film structure:

A1/B1/A1/B1/A1

- The polymer B1 is an ionomer resins based on ethylene (Surlyn 1650 from DuPont)

Using the same process as in example 1, a primary tube with the following layer thickness distribution is produced:

A1 = 135 μm , B1 = 65 μm , A1 = 90 μm , B1 = 65 μm , A1 = 135 μm .

The biaxially stretched, heat treated tubular film has a total layer thickness of 54 μm .

The flat lying width fluctuation of the flat lying tubular films is less than 1.4 mm over an observation period of 30 minutes.

A lower weights loss (0.3 wt-%) due to the evaporation of water during 20 days of storage is as expected observed in the subsequent comparative application technical tests.

In other respects, this film structure achieves equally good results regarding its filling behavior and the absence of folds as that from examples 1 and 2.

Example 4

An olefinic copolymer is inserted between the different PA layers based on example 2. The following film structure is thereby obtained (from the outside in):

A1/B1/A2/B1/A3

Using the same process as in the aforementioned examples, a primary tube with the following layer thickness distribution is produced:

A1 = 135 μm , B1 = 67 μm , A2 = 90 μm , B1 = 67 μm , A3 = 135 μm .

The biaxially stretched, heat treated tubular film has a total layer thickness of 55 μm .

The flat lying width fluctuation of the flat lying tubular films is less than 1.5 mm over an observation period of 30 minutes.

A lower weights loss (0.2 wt-%) due to the evaporation of water during 20 days of storage is as expected observed in the subsequent comparative application technical tests.

The summary of the application technical results is listed in Table 1.

Comparison example

A monolayer, biaxially stretched tubular film of PA 6 (A1) was produced based on example 1. The lower barrier effect of this film sample was in particular noticeable during the application technical testing.

Table for the examples from patent draft No. 1

| Ex. No. | Film structure (from the outside in) | Evaluation of the film by application technical tests | | | |
|---------|--|---|-----------------------------------|--------------------|--------------|
| | | "Fit" of the film after filing | After the film "sits" for 20 days | Cold storage | |
| | | | | Weight loss (wt-%) | Meat discol. |
| 1 | PA6/PA6/PA6/PA6/PA6 | Smooth and tight | Not very wrinkled | 1.2 | none |
| 2 | PA6.66/PA6.66/arom.PA/PA6/PA6 | Smooth and tight | Smooth | 1.0 | none |
| 3 | PA6/ionomer/PA6/ionomer/PA6 | Smooth and tight | Smooth and tight | 0.3 | none |
| 4 | PA6.66/ionomer/arom. PA6 / ionomer/PA6 | Smooth and tight | Smooth and tight | 0.2 | none |
| Cmp | | Smooth and tight | Wrinkled | 1.4 | visible |

Claims

- At least five-layer co-extruded, biaxially stretched tubular film for the wrapping of contents packed in the liquid or pasty state, in particular foodstuffs, which during and/or after filling undergo a heat treatment, characterized in that said tubular film is constructed from at least 3 layers containing PA which form the core layer, the inner layer and the outer layer, and in that olefinic (co)polymer layers are arranged between these PA layers.
- Tubular film according to Claim 1, characterized in that its three PA layers consist of aliphatic polyamide such as PA 6, PA 11, PA 12, PA 66, PA 6.66, PA 6.8, PA 6.9, PA 6.10, PA 6.11, PA 6.12, a copolymer consisting of the monomer units contained therein or a mixture of the named aliphatic polyamides.
- Tubular film according to Claims 1 to 2, characterized in that its three PA layers contain 70 to 95 wt-% of an aliphatic polyamide and/or copolyamide and/or mixtures of the same and at least one
(partially) aromatic PA and/or
olefinic (co)polymer (EVA, EVOH, ionomer resin, acid-modified olefin (co)polymers)
and/or (co)polyester

in quantities from at least 5 to at most 30 wt-%, relative to the total weight of the polymer mixture.
- Tubular film according to Claims 1 to 3, characterized in that the middle and/or inner layer of the three PA tubular-film layers consists of a partially aromatic PA.
- Tubular film according to Claim 4, characterized in that the partially aromatic PA is produced by polycondensation of meta-xylylene diamine and adipic acid.
- Tubular film according to one of the preceding claims, characterized in that the olefinic layers contain EVOH or typical adhesion promoters based on ethylene and/or propylene.

NOTE: This is a machine assisted translation by Beutel Consultants, Inc.

Beutel Consultants, Inc. shall not in any circumstances be liable or responsible for the completeness and accuracy of any Beutel Consultants translation and will not be liable for any direct or indirect consequential or economic loss or loss of profit resulting directly or indirectly from the use of any translation by Beutel Consultants.

#####

Job : 176
Date: 6/30/2004
Time: 10:46:55 AM



David V Mesaros/SE/DuPont
06/30/2004 10:44 AM

To Ann F Griffith/AE/DuPont@DuPont
cc
bcc
Subject Re: Survey for Six Sigma Project -- Please Respond by Friday July 9

1. What are your needs (essential elements) regarding a process to correlate the HTN patent estate with commercial products and candidates of the HTN business within EP? (By "correlate" we mean identifying which patents provide legal coverage for products, whether products are adequately protected by patents, etc.)

Since I am no longer an HTN product developer, I don't see myself having needs to correlate HTN patents with products. Even when I was in such a role, the focus was to first develop a product then consider the IP implications fairly narrowly around that development.

2. What are your desires (not essential elements but helpful if can incorporate into the improved process) regarding the process to correlate the HTN patent estate with commercial products and candidates of the HTN business within EP?

My primary focus now is competitive patent estates and looking for IP opportunities for EP. An end product that correlates HTN patents with products could play a minor role in my work by improving perspective of EP's patent estate versus our competitors. It also leads to questions about correlating competitor patent estates with their product portfolios.

3. How well does the current process (the patent maintenance reviews referred to above) meet your needs?

I am unaware of the details around the current process of patent maintenance reviews. I have not been involved, but that is to be expected for not having authored any patents that might need to be reviewed.

4. Can you identify any shortcomings to the current process?

No, but for the reason noted in my answer to question 3.

5. Can you identify any aspects of the current process that require immediate attention to contain a problem, eg if we fail to resolve the situation quickly the issue could have immediate negative consequences to HTN?

No.

6. Are there any other comments you would like to make that would benefit this project?

At some point the scope of this effort will need to look beyond estate maintenance based on a correlation of DuPont patents with products and development programs. Recent discussions about EP's IP strategy indicate a desire to also use patents to block the efforts of competitors, serve as bargaining chips, and provide licensing opportunities. So decisions on the maintenance of particular patents must consider much more than whether EP has products based on them. Perhaps this is already being considered, but the scope of this GB project is intentionally confined to a single aspect of the larger scope.